



# Identification of $\text{Fe}^{3+}$ – $\text{Li}^+$ complexes in ZnO by means of high-frequency EPR/ENDOR spectroscopy



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## ABSTRACT

Theoretical prediction of a high Curie temperature in ZnO doped with Mn, Fe, and other transition metals has stimulated the investigation of these materials by many research groups. Although charge-compensated  $\text{Fe}^{3+}$  centers in ZnO:Fe have been observed by means of EPR and have been known for decades, conclusions on the chemical nature of these defects are still contradictory. Originally, these centers were treated as  $\text{Fe}^{3+}$ – $\text{Li}^+$  complexes with both ions occupying adjacent cationic sites. Recently, however, the centers were interpreted as a substitutional  $\text{Fe}^{3+}$  ion with a vacancy at an adjacent zinc or oxygen site ( $\text{Fe-V}_{\text{Zn}}$  or  $\text{Fe-V}_{\text{O}}$ ). In order to determine the chemical nature of the impurity associated with  $\text{Fe}^{3+}$ , electron-nuclear double resonance (ENDOR) spectroscopy was used. ENDOR measurements reveal NMR transitions corresponding to nuclei with  $g$ -factor  $g_N = 2.171$  and spin  $I = 3/2$ . This unambiguously shows presence of Li as a charge compensator and also resolves contradictions with the theoretical prediction of the  $\text{Fe-V}_{\text{O}}$  formation energy. The electric field gradients at the  $^7\text{Li}$  nuclei (within the  $\text{Fe}^{3+}$ – $\text{Li}^+$  complexes) were estimated to be significantly lower than the gradient at undistorted Zn sites.

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## 1. Introduction

ZnO is a II–VI semiconductor with a wide direct band gap of about 3.3 eV at room temperature. Due to its unique optical, electrical, and mechanical properties, it has recently regained a lot of attention as a material for UV light-emitting diodes, a transparent conducting oxide for photovoltaic applications, a radiation hard material, etc. [1,2]. Much effort is also made towards developing diluted magnetic semiconductors based on a theoretically predicted high Curie temperature in ZnO doped with high concentrations of transition metals (TM) [3,4].

Nominally undoped ZnO crystals often contain TM ions, which incorporate into the material at substitutional sites during the crystal growth process. Electron paramagnetic resonance (EPR) has been widely used to study various impurities in ZnO [5,6]. In ZnO crystals containing Fe, EPR experiments reveal the spectrum of the trigonal  $\text{Fe}_{\text{Zn}}$  center [7,8], as well as multiple additional signals assigned to charge-compensated  $\text{Fe}^{3+}$  [7,9–11]. However, conclusions on the chemical nature of the charge-compensated Fe centers are contradictory. The older work [9] treats the centers as Fe–Li complexes, whereas authors of a more recent research [10] interpret the centers as an  $\text{Fe}^{3+}$  ion with a vacancy at an adjacent zinc or oxygen site ( $\text{Fe-V}_{\text{Zn}}$ ,  $\text{Fe-V}_{\text{O}}$ ). As noted by the authors,

the latter model contradicts the theoretical prediction [12] that formation of the  $\text{Fe-V}_{\text{O}}$  complex is not energetically favored.

The hydrothermal growth method is commonly used for ZnO, since it allows for growing large single crystals. However, these crystals inevitably contain significant amounts of Li [13], in addition to TM ions. Therefore, establishing the real nature of the complex will contribute to a better understanding of incorporation of Fe and Li into the ZnO lattice and should resolve (or confirm) contradictions with the theoretical predictions concerning the  $\text{Fe-V}_{\text{O}}$  formation energy.

Since no hyperfine (HF) splitting is observed in the EPR spectra of the charge-compensated Fe centers, it is not possible to identify the chemical nature of the complex by means of conventional EPR. It should be supplemented with modern multiple resonance techniques. Electron-nuclear double resonance (ENDOR) has been successfully used to investigate numerous defects in ZnO single- and nanocrystals [14–17]. This method reveals interactions of the electrons with surrounding magnetic nuclei. Therefore, if  $\text{Fe}^{3+}$  ions form complexes with other elements (e.g., Li), this interaction should give rise to signals in ENDOR spectra that will correspond to the nuclear  $g$ -factor and spin of the charge compensating impurity.

## 2. Experimental details

ZnO used in this investigation was a nominally undoped hydrothermally grown  $c$ -cut single crystal. For the EPR measurements, a

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